A Vibrational spectroscopic study of tengerite-(Y) $Y_2(CO_3)_3 \cdot 2\text{-}3H_2O$

Ray L. Frost [a•], Andrés López[a], Lina Wang [a,b], Ricardo Scholz[c], Ney Pinheiro Sampaio[d] Fernando A. N. de Oliveira[e]

[a] School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

[b] School of Chemistry and Chemical Engineering, Tianjin University of Technology, No.391, Bin Shui West Road, Xi Qing District, Tianjin, P. R. China

[c] Geology Department, School of Mines, Federal University of Ouro Preto, Campus Morro do Cruzeiro, Ouro Preto, MG, 35,400-00, Brazil

[d] NanoLab, REDEMAT, School of Mines, Federal University of Ouro Preto, Campus Morro do Cruzeiro, Ouro Preto, MG, 35,400-00, Brazil

[e] Federal Institute of Minas Gerais, Campus Ouro Preto, Ouro Preto, MG, 35,400-000, Brazil

Abstract

The mineral tengerite-(Y) has been studied by vibrational spectroscopy. Multiple carbonate stretching modes are observed and support the concept of non-equivalent carbonate units in the tengerite-(Y) structure. Intense sharp bands at 464, 479 and 508 cm^{-1} are assigned to YO stretching modes. Raman bands at 765 and 775 cm^{-1} are assigned to the CO_3^{2-} ν_4 bending modes and Raman bands at 589, 611, 674 and 689 cm^{-1} are assigned to the CO_3^{2-} ν_2 bending modes. Multiple Raman and infrared bands in the OH stretching region are observed, proving the existence of water in different molecular environments in the structure of tengerite-(Y).

Key words: tengerite-(Y), carbonate, hydroxyl, Infrared and Raman spectroscopy

• Author to whom correspondence should be addressed (r.frost@qut.edu.au)
P +61 7 3138 2407 F: +61 7 3138 1804

Introduction

The mineral tengerite-(Y) $Y_2(CO_3)_3 \cdot 2\text{-}3H_2O$ [1, 2] was originally named by James D. Dana and George J. Brush in 1868 after C. Tenger, Swedish chemist who described the mineral in 1838 along with Adolf Ferdinand Svanberg, but the new mineral was left unnamed. Synthetic analogs of tengerite-(Y) and compositionally related minerals have been made [3-6].Tengerite-(Y) is not well-described and subsequently lokkaite-(Y) $Ca(Y,Gd,Nd,Dy)_4(CO_3)7 \cdot 9H_2O$ and kimuraite-(Y) $Ca(Y,Nd)_2(CO_3)4 \cdot 6H_2O$ were described as new and independent species.

Miyawaki et al. [2, 7] redefined tengerite-(Y) in 1993. Tengerite-(Y) is orthorhombic with point group *mm2* [2]. Its space group is $Bb2_1m$ with a = 6.078(4)Å, b = 9.157(2)Å, c = 15.114(6)Å and Z = 4. The mineral is normally found as thin coatings and powders with crystal rosettes to 1 mm. Investigation of type material showed that "tengerite-(Y)" from Ytterby was actually lokkaite-(Y). Tengerite-(Y) as redefined does occur at Ytterby, but is much rarer than lokkaite-(Y). Miyawaki et al. [2] did not describe any of the physical properties of the redefined mineral. There is a need to study the mineral tengerite's physical properties, including its vibrational spectra.

The vibrational spectroscopic characterization of REE carbonates can be an important tool in the mineral exploration. In this work, samples of the yttrium carbonate tengerite-(Y) from Paratoo mine, South Australia has been carried out. Studies include spectroscopic characterization of the structure with infrared and Raman. Chemical study via Scanning electron microscope (SEM) was applied in the mineral characterization.

Experimental

Samples description and preparation

The tengerite-(Y) sample studied in this work originated from Paratoo copper mine, Yunta, Olary Province, South Australia, Australia.
The compositions have been reported by Anthony et al. (page 698) [8]. The sample was incorporated to the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAD-048. The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. Qualitative and

semiquantitative chemical analyses via SEM/EDS were applied to the mineral characterization. .

Scanning electron microscopy (SEM)

Experiments and analyses involving electron microscopy were performed in the Center of Microscopy of the Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil (http://www.microscopia.ufmg.br).

Tengerite-(Y) crystals were coated with a 5nm layer of evaporated carbon. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment. Qualitative and semi-quantitative chemical analyses in the EDS mode were performed with a ThermoNORAN spectrometer model Quest and were applied to support the mineral characterization.

Raman microprobe spectroscopy

Crystals of tengerite-(Y) were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarized light at 633 nm and collected at a nominal resolution of 2 cm^{-1} and a precision of ± 1 cm^{-1} in the range between 200 and 4000 cm^{-1}. Repeated acquisitions on the crystals using the highest magnification (50x) were accumulated to improve the signal to noise ratio of the spectra. Raman Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. The Raman spectrum of at least 10 crystals was collected to ensure the consistency of the spectra.

An image of the tengerite-(Y) crystals measured is shown in the supplementary information as Figure S1. Clearly the crystals of tengerite-(Y) are readily observed, making the Raman spectroscopic measurements readily obtainable.

Infrared spectroscopy

Infrared spectra of tengerite-(Y) were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm^{-1}

range were obtained by the co-addition of 128 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentzian-Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Lorentzian-Gaussian ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

Results and discussion

Vibrational spectroscopy

Spectroscopy of carbonate anion

It is important to understand the vibrational spectroscopy of the carbonate anion in different molecular environments. Nakamoto *et al.* first published and tabulated the selection rules for unidenate and bidentate anions including the carbonate anion [9-11]. The free ion, CO_3^{2-} with D_{3h} symmetry exhibits four normal vibrational modes; a symmetric stretching vibration (ν_1), an out-of-plane bend (ν_2), a doubly degenerate asymmetric stretch (ν_3) and another doubly degenerate bending mode (ν_4). The symmetries of these modes are A_1' (R) + A_2'' (IR) + E′ (R, IR) + E′′ (R, IR) and occur at 1063, 879, 1415 and 680 cm^{-1} respectively. Generally, strong Raman modes appear around 1100 cm^{-1} due to the symmetric stretching vibration (ν_1), of the carbonate groups, while intense IR and weak Raman peaks near 1400 cm^{-1} are due to the antisymmetric stretching mode (ν_3). Infrared modes near 800 cm^{-1} are derived from the out-of-plane bend (ν_2). Infrared and Raman modes around 700 cm^{-1} region are due to the in-plane bending mode (ν_4). This mode is doubly degenerate for undistorted CO_3^{2-} groups [10]. As the carbonate groups become distorted from regular planar symmetry, this mode splits into two components [10]. Infrared and Raman spectroscopy provide sensitive test for structural distortion of CO_3^2.

Vibrational spectroscopy of tengerite-(Y)

The Raman spectrum of tengerite-(Y) in the 100 to 4000 cm^{-1} spectral range is displayed in Figure 1a. This spectrum shows the position and relative intensities of the Raman bands. It is noted that there are large parts of the spectrum where no intensity or minimal intensity is observed. Thus, the spectrum is subdivided into subsections depending upon the type of vibration being studied. The infrared spectrum of tengerite-(Y) in the 500 to 4000 cm^{-1} spectral region is shown in Figure 1b. This figure shows the position of the infrared bands and their relative intensities. This spectrum displays the position and relative intensities of the infrared bands. As for the Raman spectrum, there are parts of the spectrum where little or no intensity is observed.

The Raman spectrum of tengerite-(Y) over the 950 to 1450 cm^{-1} spectral range is reported in Figure 2a. An intense Raman band at 1100 cm^{-1} with shoulder bands at 1091 and 1114 cm^{-1} is assigned to the CO_3^{2-} ν_1 symmetric stretching mode. The band at 1091 cm^{-1} is attributed to a hot band. The band at 1114 cm^{-1} is of a very low intensity. A second band is noted at 1067 cm^{-1} with low intensity bands on the low wavenumber side at 1038 and 1062 cm^{-1}. This band is also assigned to the CO_3^{2-} ν_1 symmetric stretching mode. Thus, there appears to be bands attributable to two symmetric stretching modes of carbonate. One interpretation of this fact is that there are two distinct non-equivalent carbonate units in the structure of tengerite-(Y). Two broad bands at 1334 and 1392 cm^{-1} are attributed to the CO_3^{2-} ν_3 antisymmetric stretching mode.

The infrared spectrum of tengerite-(Y) over the 650 to 1250 cm^{-1} spectral range is illustrated in Figure 2b. In comparison with the Raman spectrum, the infrared spectrum is broad with overlapping component bands. Infrared bands are resolved at 985, 1003, 1029, 1051, 1115 and 1137 cm^{-1}. The first two bands may be assigned to the CO_3^{2-} ν_1 symmetric stretching mode. The bands at 1029, 1051, 1115 and 1137 cm^{-1} are attributed to the CO_3^{2-} ν_3 antisymmetric stretching mode.
It would appear to be unreasonable to assign individual component bands. The infrared bands at 890, 912 and 935 cm^{-1} are probably due to water librational modes.

The Raman spectrum of tengerite-(Y) over the 350 to 850 cm^{-1} spectral range is reported in Figure 3a. The Raman bands at 765 and 775 cm^{-1} are assigned to the CO_3^{2-} ν_4 bending modes. The Raman spectrum shows two bands which have been deconvoluted. This spectral profile may contain additional bands. In the infrared spectrum (Figure 3b), the series of low

intensity bands at 728, 751, 777, and 798 cm^{-1} may also be attributed to this vibrational mode. The series of Raman bands at 589, 611, 674 and 689 cm^{-1} are assigned to the CO_3^{2-} ν_2 bending modes. In the infrared spectrum (Figure 2b), the low intensity bands at 678 and 695 cm^{-1} is also attributed to this vibrational mode. What are quite interesting are the sharp Raman bands at 464, 479 and 508 cm^{-1}. The position of these bands is well below where any carbonate bands might be expected. These bands are assigned to Y-O stretching vibrational modes. The observation of three bands supports the concept that the YO bond lengths are not equal, thus resulting in three bands. The Raman bands at 355, 398, 408 and 417 cm^{-1} may be attributed to O-Y-O bending modes. The observation of multiple bands again supports the fact that the YO bonds are not identical. The Raman spectrum of tengerite-(Y) over the 100 to 350 cm^{-1} spectral range is reported in Figure 3b. Raman bands are found at 109, 115, 145, 161, 186, 195, 208, 239, 252, 264, 270, 291, 300 and 329 cm^{-1}. These bands are simply assigned to lattice vibrational modes.

The Raman spectrum of tengerite-(Y) over the 2400 to 3800 cm^{-1} spectral range is shown in Figure 4a. The spectrum is complex with overlapping bands found at 2657, 2789, 2920, 3047, 3241, 3281 and 3367 cm^{-1}. These bands are assigned to water stretching vibrations. The infrared spectrum of tengerite-(Y) over the 2800 to 3800 cm^{-1} spectral range is shown in Figure 4b. As for the Raman spectrum, the infrared spectrum shows complexity. Infrared bands are resolved at 2942, 3050, 3236, 3429 and 3578 cm^{-1}. These bands are ascribed to water stretching vibrations. The infrared bands at 3618, 3621, 3649, 3669 and 3692 cm^{-1} are assigned to the stretching vibrations of the OH units of kaolinite. The tengerite-(Y) is found as a coating upon a clay background matrix, so it's not unexpected to find the spectrum of tengerite superimposed upon the spectrum of kaolinite.

The Raman spectrum of tengerite-(Y) over the 1450 to 1750 cm^{-1} spectral range is shown in Figure 5a. Raman bands in this spectral region are attributable to the bending modes of water. Raman bands are observed at 1592, 1618, 1637 and 1689 cm^{-1}. The observation of multiple bands in this spectral region is in harmony with the number of Raman bands in the OH stretching region (Figure 4a). These bands show that water exists in the structure of tengerite-(Y) in different molecular environments with differing bond strengths. The infrared spectrum of tengerite-(Y) over the 1300 to 1800 cm^{-1} spectral range is shown in Figure 4b. Infrared bands found at 1587, 1632 and 1674 cm^{-1} are assigned to water bending modes. The number of infrared bands in this spectral region is in harmony with the number of infrared

bands in the OH stretching region. The series of infrared bands at 1354, 1391, 1422, 1467 and 1493 cm^{-1} are attributed to the CO_3^{2-} ν_3 antisymmetric stretching mode.

Studies have shown a strong correlation between OH stretching frequencies and both O···O bond distances and H···O hydrogen bond distances [12-15]. Libowitzky (1999) showed that a regression function can be employed relating the hydroxyl stretching frequencies with regression coefficients better than 0.96 using infrared spectroscopy [15]. The function is described as: $\nu_1 = (3592 - 304) \times 109^{\frac{-d(O-O)}{0.1321}}$ cm^{-1}. Thus OH---O hydrogen bond distances may be calculated using the Libowitzky empirical function. The values for the OH stretching vibrations detailed above provide hydrogen bond distances of 0.2735 pm (3279 cm^{-1}), 0.27219 pm (3237 cm^{-1}). Frueh and Golightly suggested some hydrogen bonding exists for tengerite-(Y) [17]. The values calculated here, support the concept of strong hydrogen bonding between the OH units and the carbonate anions in the tengerite-(Y) structure.

Conclusions

The mineral tengerite-(Y) is one of several related minerals of the tengerite mineral group including lokkaite-(Y) $Ca(Y,Gd,Nd,Dy)_4(CO_3)7{\cdot}9H_2O$, kimuraite-(Y) $Ca(Y,Nd)_2(CO_3)4{\cdot}6H_2O$ and hizenite-Y $Ca_2Y_6(CO_3)_{11}{\cdot}14H_2O$. These minerals remain ill-defined and often are confused one with the other. The physical properties of the mineral tengerite-(Y) have not been fortcoming. In this work the mineral tengerite-(Y) from South Australia was analysed using vibrational spectroscopy.

The mineral tengerite-(Y) is characterised by multiple CO_3^{2-} stretching and bending modes, giving credence to the existence of more than one non-equivalent unit in the tengerite-(Y) structure. The Raman and infrared spectrum of tengerite in the water OH stretching and water bending region shows multiple bands thus providing evidence for the existence of water in the structure of tengerite-(Y) in different molecular environments with different hydrogen bond strengths.

Acknowledgements

The financial and infra-structure support of the Discipline of Nanotechnology and Molecular Science, Science and Engineering Faculty of the Queensland University of Technology, is

231 gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the
232 instrumentation.
233

References

[1] T. Iimori, Scientific Papers of the Institute of Physical and Chemical Research (Japan), 34 (1938) 832-841

[2] R. Miyawaki, J. Kuriyama, I. Nakai, Amer. Min. 78 (1993) 425-432.

[3] K. Nagashima, H. Wakita, A. Mochizuki, Bull. Chem. Soc. Jap. 46 (1973) 152-156.

[4] J.A.K. Tareen, T.R.N. Kutty, K.V. Krishnamurty, J. Cryst. Growth, 49 (1980) 761-765.

[5] H. Wakita, Bull. Chem. Soc. Jap. 51 (1978) 2879-2881.

[6] H. Wakita, K. Nagashima, Bull. Chem. Soc. Jap. 45 (1972) 2476-2479.

[7] R. Miyawaki, I. Nakai, Kidorui, 23 (1993) 1-21.

[8] J.W. Anthony, R.A. Bideaux, K.W. Bladh, M.C. Nichols, Handbook of Mineralogy, Mineral Data Publishing, Tuscon, Arizona, USA, 2003.

[9] K. Nakamoto, Bunko Kenkyu, 5 (1957) 3-13.

[10] K. Nakamoto, J. Fujita, S. Tanaka, M. Kobayashi, J. Amer. Chem. Soc. 79 (1957) 4904-4908.

[11] Kazuo Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part A: Theory and Applications in Inorganic Chemistry , 6th edn. (Wiley, John Wiley & Sons, Inc., Hoboken, 2009).

[12] J. Emsley, Very strong hydrogen bonding., Chem. Soc. Rev. 9 (1980) 91-124.

[13] H. Lutz, Structure and Bonding (Berlin, Germany), 82 (1995) 85-103.

[14] W. Mikenda, J. Mol. Struc. 147 (1986) 1-15.

[15] A. Novak, Structure and Bonding (Berlin), 18 (1974) 177-216.

[16] E. Libowitsky, Monat. Chem.130 (1999) 1047-1049.

[17] A.J. Frueh, Jr., J.P. Golightly, Can. Min. 9 (1967) 51-56.

List of figures

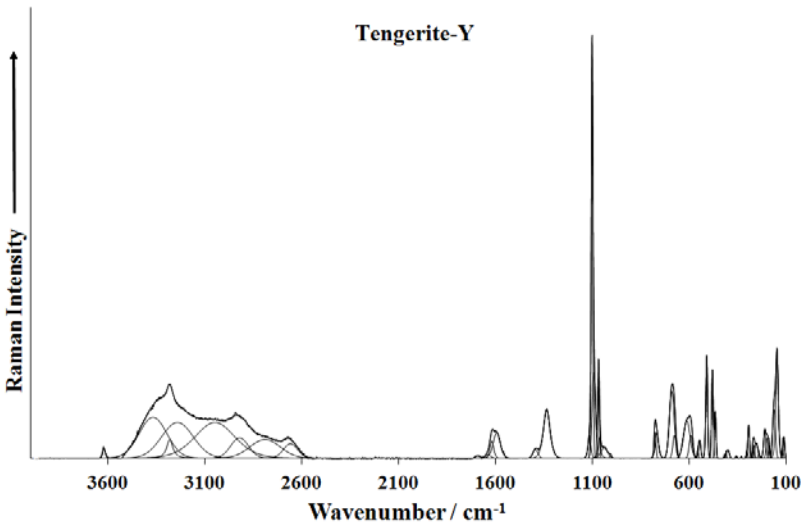
Figure 1 (a) Raman spectrum of tengerite-(Y) over the 100 to 4000 cm^{-1} spectral range (upper spectrum) (b) Infrared spectrum of tengerite-(Y) over the 500 to 4000 cm^{-1} spectral range (lower spectrum)

Figure 2(a) Raman spectrum of tengerite-(Y) over the 800 to 1400 cm^{-1} spectral range (upper spectrum) (b) Infrared spectrum of tengerite-(Y) over the 650 to 1150 cm^{-1} spectral range (lower spectrum)

Figure 3 (a) Raman spectrum of tengerite-(Y) over the 300 to 800 cm^{-1} spectral range (b) Raman spectrum of tengerite-(Y) over the 100 to 300 cm^{-1} spectral range

Figure 4 (a) Raman spectrum of tengerite-(Y) over the 2600 to 3800 cm^{-1} spectral range (upper spectrum) (b) Infrared spectrum of tengerite-(Y) over the 2500 to 3800 cm^{-1} spectral range (lower spectrum)

Figure 5 (a) Raman spectrum of tengerite-(Y) over the 1400 to 1800 cm^{-1} spectral range (b) Infrared spectrum of tengerite-(Y) over the 1200 to 1700 cm^{-1} spectral range



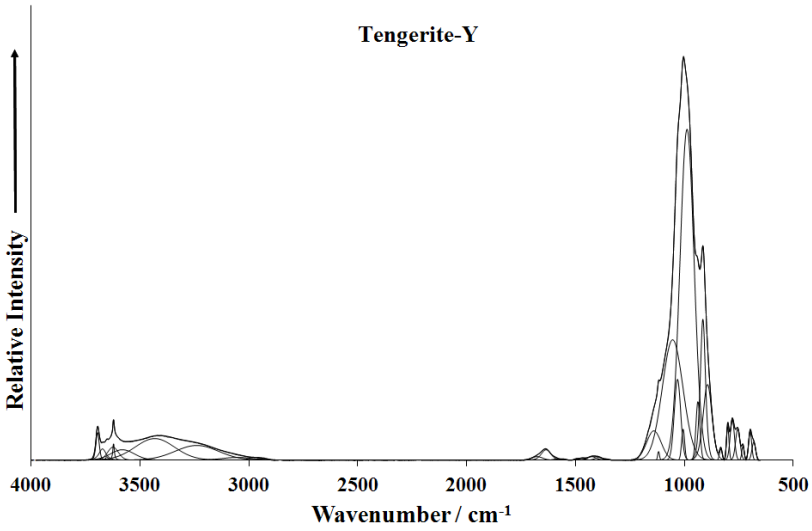
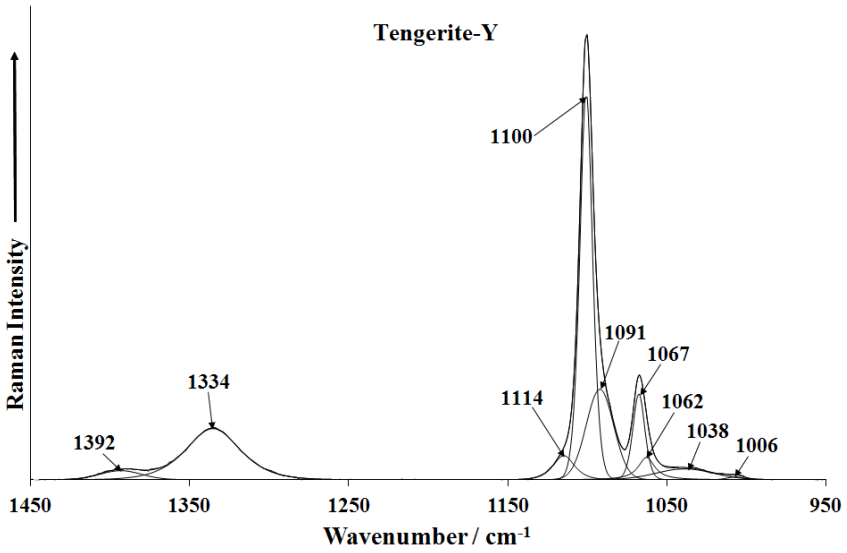


Figure 1 (a) Raman spectrum of tengerite-(Y) over the 100 to 4000 cm^{-1} spectral range (upper spectrum) (b) Infrared spectrum of tengerite-(Y) over the 500 to 4000 cm^{-1} spectral range (lower spectrum)

313



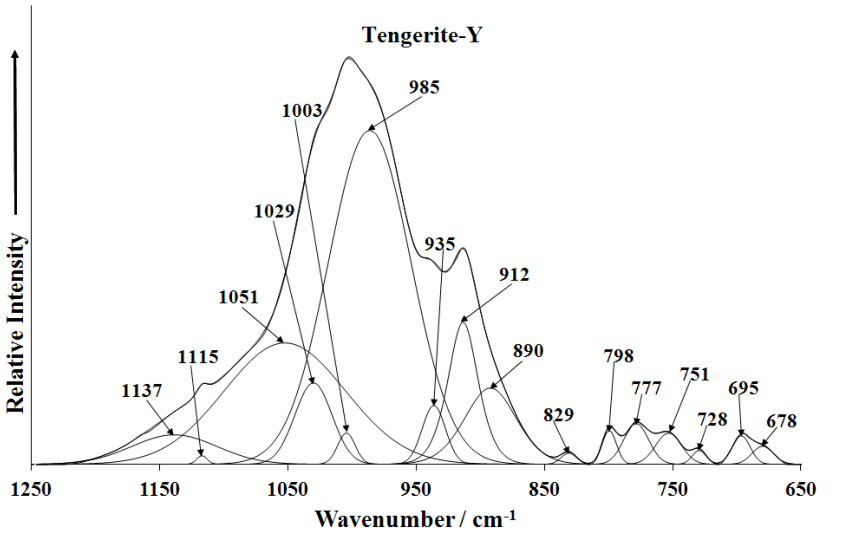
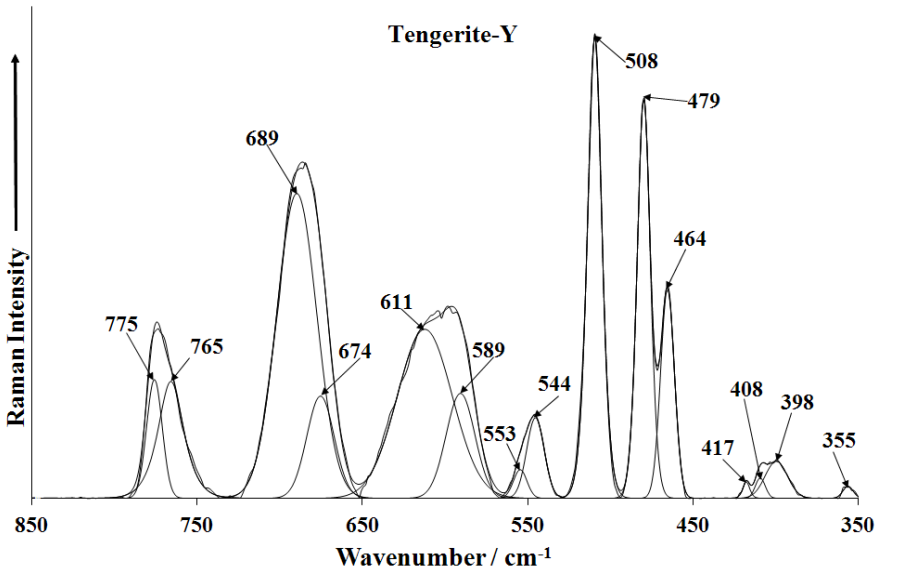


Figure 2a Raman spectrum of tengerite-(Y) (upper spectrum) in the 950 to 1450 cm^{-1} spectral range and Figure 2b infrared spectrum of tengerite-(Y) (lower spectrum) in the 650 to 1250 cm^{-1} spectral range

314

315



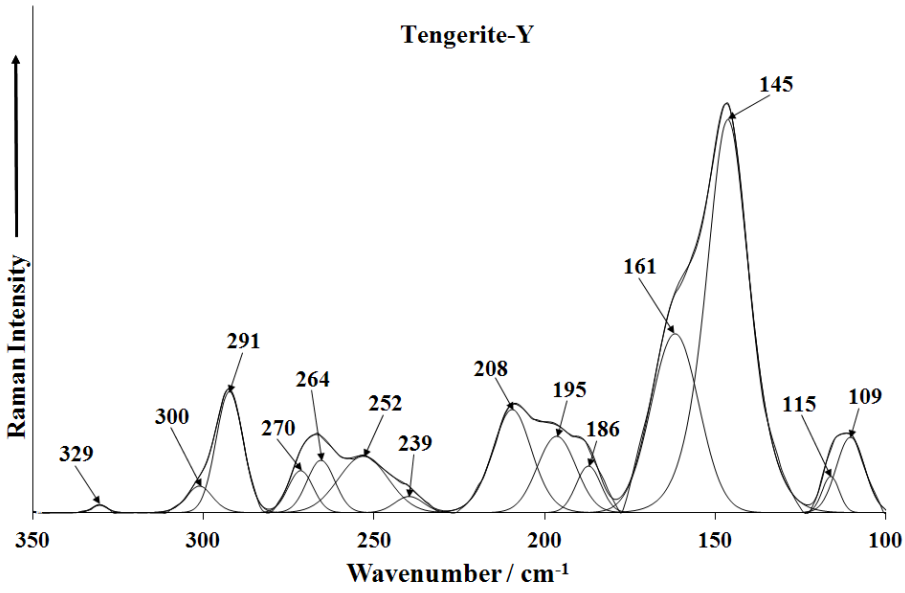
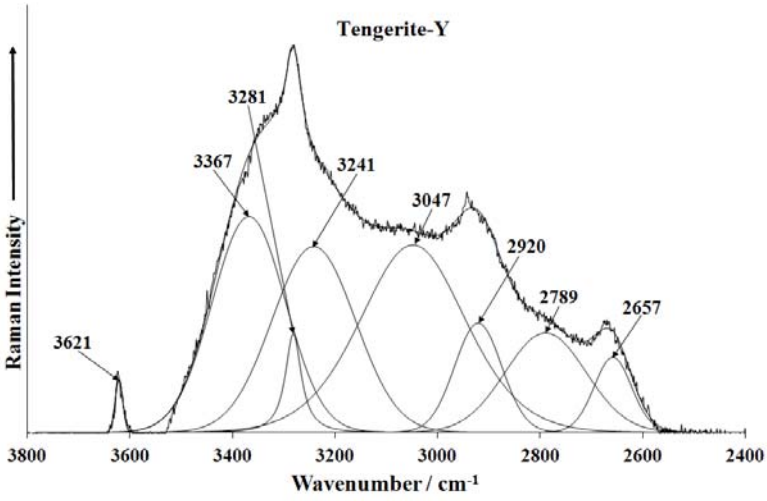


Figure 3a Raman spectrum of tengerite-(Y) (upper spectrum) in the 300 to 800 cm^{-1} spectral range and Figure 3b Raman spectrum of tengerite-(Y) (lower spectrum) in the 100 to 300 cm^{-1} spectral range

316

317



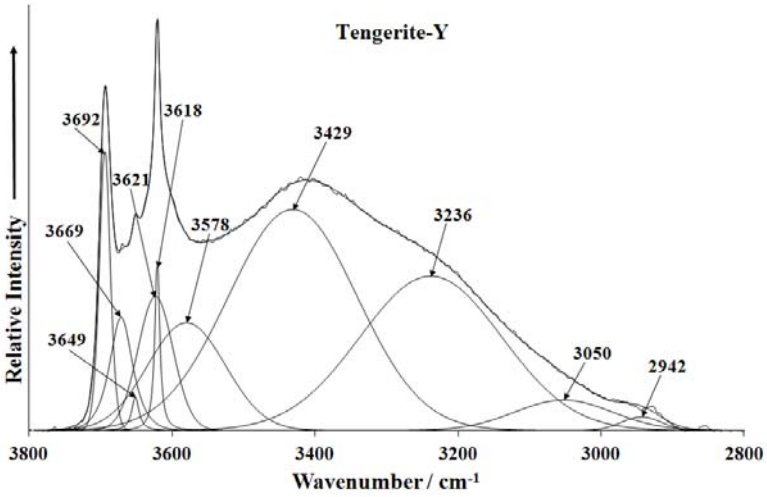
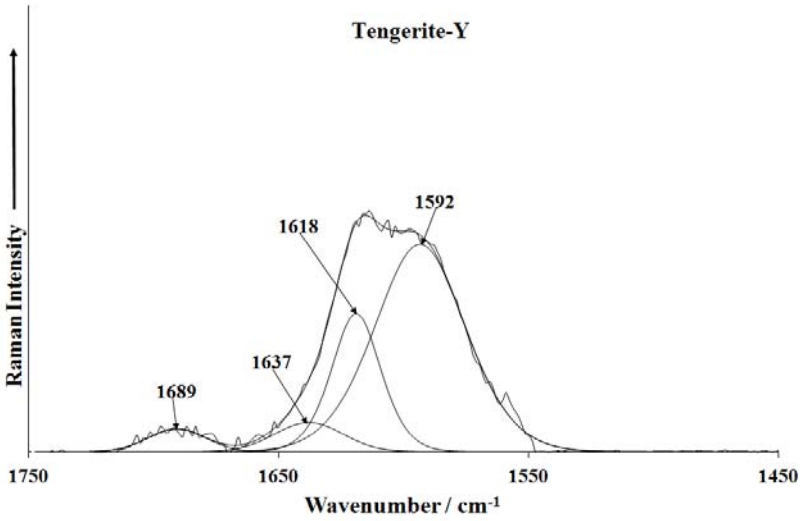


Figure 4a Raman spectrum of tengerite-(Y) (upper spectrum) in the 2600 to 3800 cm^{-1} spectral range and Figure 4b infrared spectrum of tengerite-(Y) (lower spectrum) in the 2800 to 3500 cm^{-1} spectral range

318

319

320



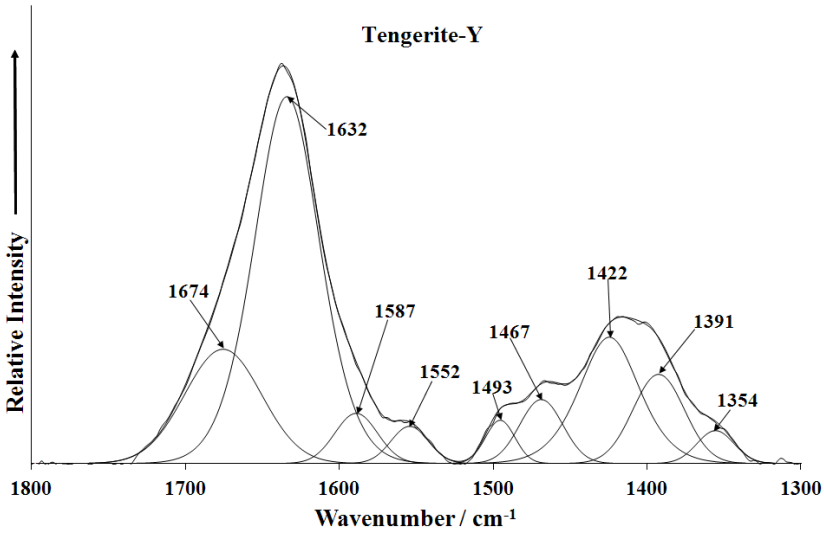


Figure 5a Raman spectrum of tengerite-(Y) (upper spectrum) in the 1400 to 1800 cm^{-1} spectral range and Figure 5b infrared spectrum of tengerite-(Y) (lower spectrum) in the 1200 to 1700 cm^{-1} spectral range

321

322

323

324
325